

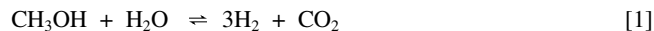
LOW TEMPERATURE STEAM REFORMING OF METHANOL OVER LAYERED DOUBLE HYDROXIDES

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Introduction

Catalytic steam reforming of methanol [eqn. 1] is a well-established process for the production of hydrogen:



This process is especially important in applications such as proton exchange membrane (PEM) fuel cells, which generate electrical power by electrochemical oxidation of hydrogen with atmospheric oxygen.¹ The use of methanol as an on-board hydrogen source is attractive for fuel-cell engines for transportation applications, due to its safe handling, low cost, and ease of synthesis from a variety of feedstocks (e.g., biomass, coal, and natural gas).² Layered double hydroxides are a class of anionic clays that contain positively charged brucite $\text{Mg}(\text{OH})_2$ -like layers where several Mg^{2+} ions are substituted by trivalent ions such as Al^{3+} ; the excess positive charge is counterbalanced by anions in the interlayer plus water molecules.³ LDHs are well-suited as catalysts due to their high surface area, basic properties, high metal dispersion, and ability to be prepared with various redox active cations.⁴

In this work, we have prepared layered double hydroxide (LDH) catalysts containing different metal combinations including Cu/Al, Co/Al, Ni/Al, and Mg/Al. The LDHs were prepared by a co-precipitation method at constant pH. The LDHs were characterized by X-ray diffraction (XRD), temperature-programmed reduction (TPR), and thermal gravimetric analyses (TGA). The catalysts were tested for steam reforming of methanol at temperatures between 150-400 °C at atmospheric pressure.

Experimental

Catalyst Preparation. LDHs were prepared using a standard co-precipitation technique similar to that reported by Sanchez Valente, et al.⁵ All syntheses were performed at room temperature in air. The LDHs were synthesized by drop-wise addition of an aqueous solution containing 2 M NaOH and 0.5 M Na_2CO_3 to an aqueous $\text{M}^{2+}/\text{M}^{3+}$ nitrate salt solution with vigorous stirring. The ratio $\text{M}^{2+}/\text{M}^{3+} = 3$ ($\text{M}^{2+} = 0.75$ M, $\text{M}^{3+} = 0.25$ M). The NaOH/ Na_2CO_3 solution was added using a pH stat instrument (718 Stat Titrino, Metrohm), which allows precise pH control. The pH = $9.00 \pm .02$ in all syntheses, except for the Cu/Al LDH, which was synthesized at a pH = $8.00 \pm .02$. The $\text{M}^{2+}/\text{M}^{3+}$ solution was added at a constant rate (0.4 ml/min) using a 776 Dosimat (Metrohm) instrument. After addition of all reagents, the solution was heated overnight at 65 °C with stirring. The sample was then filtered, washed several times with deionized water, and dried in air at 80 °C for 18 h. No further treatments were performed on the LDHs prior to catalytic testing.

Characterization techniques. XRD was measured with a Rigaku Miniflex+ instrument (30 kV, 15 mA) using $\text{CuK}\alpha$ radiation, a 0.05° step size, and a 2° 2θ /min scan rate from 5 – 65° 2θ . TPR measurements were made on an Altamira AMI-1 equipped with a thermal conductivity detector (TCD). The sample (0.100 g) was reduced with 4% H_2/Ar from 50–800 °C at a rate of 5 °C/min using a

flow rate of 30 ml/min. Thermal gravimetric analyses were performed on a HAAKE instruments EXSTAR 6000. Samples of ~5 mg were heated at 5 °C/min in flowing N_2 (100 ml/min) from 25–800 °C. The samples were measured against an alumina reference.

Catalytic Activity. Activity tests were performed in a flow reactor system at atmospheric pressure. A 1:1 molar mixture of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ was introduced into a 0.18" x 2 cm stainless steel reactor that contained 0.150 g of the catalyst. The reactants were delivered into the catalytic reactor using a Hewlett Packard 1050 HPLC pump at a total flow rate of 0.25 ml/min. The reactor was placed in a temperature-controlled oven and experiments were performed by ramping the temperature from 150–400 °C at 1 °C/min. Prior to all experiments, the catalyst was purged with He at 150 °C for 30 min. After flowing through the reactor, the feed was passed through a condenser (chilled to -16°C) to trap out any unreacted CH_3OH and H_2O . The gaseous products were then injected into a Hewlett Packard 5890 Series II GC (GasPro GSC column, TCD detection) to measure products such as H_2 , CO_2 , CH_4 , and CO . In order to measure reactant conversion (CH_3OH and H_2O), a separate experiment was performed in which the product stream was passed directly into a Stanford Research System RGA 200 mass spectrometer.

Results and Discussion

All catalysts except the Mg/Al LDH exhibited steam reforming activity. The most active catalyst found in these studies is the Cu/Al LDH. The catalytic activity of the Cu/Al LDH is shown in Figure 1.

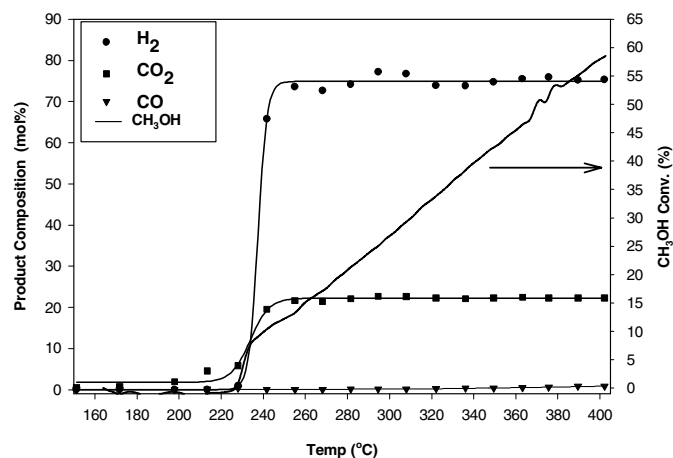


Figure 1. Catalytic activity as a function of temperature for a Cu/Al LDH.

Note that in these experiments the reactor lines are purged with He prior to the reaction, and therefore the balance of the total mol% is composed of He. The results from Figure 1 show that the Cu/Al LDH becomes catalytically active for the steam reforming of methanol at around 230 °C. As the temperature is increased, the CH_3OH conversion increases and near-stoichiometric amounts of H_2 and CO_2 are produced. With increasing conversion, the H_2/CO_2 ratio remains the same. CO_2 is the major C-containing product, however, small amounts of CO are produced as the temperature increases (0.8 mol% at 400 °C). Most likely, the CO is formed due to the reverse water-gas shift reaction, which is commonly observed with Cu-containing steam reforming catalysts.⁶

Catalytic data for Co/Al and Ni/Al LDHs are shown in Figure 2.

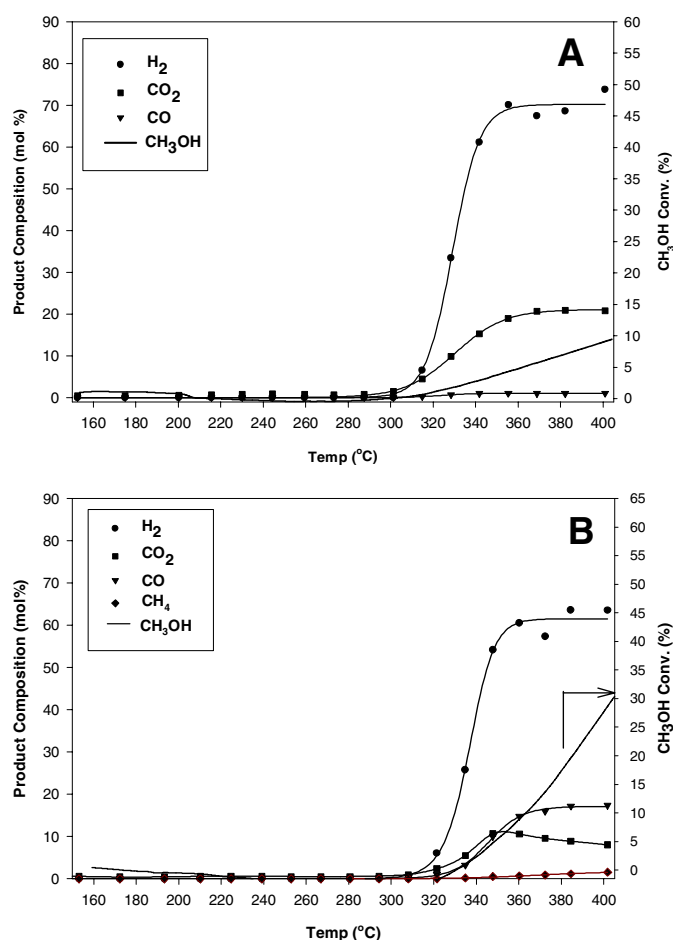


Figure 2. Catalytic activity of A) Co/Al LDH and B) Ni/Al LDH as function of temperature.

The behavior of the Co/Al LDH is similar to that observed with the Cu/Al LDH, except that the activation temperature is considerably higher (315 °C) and methanol conversion is significantly less than that of the Cu/Al LDH. As with the Cu/Al LDH, trace amounts of CO are produced as the temperature increases (1.0 mol % at 400 °C).

Results for the Ni/Al LDH differ from those of both the Cu/Al and Co/Al LDHs. As with the Co/Al LDH, the activation temperature for the Ni/Al LDH is ~320 °C. Methanol conversion is intermediate between that of the Cu/Al and Co/Al LDHs. The major product formed over the Ni/Al LDH is H₂. However, considerably less CO₂ is formed (8.0 mol % at 400 °C). The product composition indicates that a significant amount of CO is produced (17 mol % at 400 °C). This result suggests that the major reaction occurring over the Ni/Al LDH is methanol decomposition (Eq 2).



This result is consistent with literature reports, which show that Ni-containing catalysts promote methanol decomposition according to reaction [2].²

XRD studies indicate that significant structural changes occur in the LDH materials during the catalytic reactions. These changes are also reflected in significant changes in the color of the catalysts. Immediately following the catalytic reactions, XRD shows

that the Cu/Al LDH structure decomposes to a highly crystalline metallic Cu phase. This result is also consistent with literature reports, which indicate that the active species in Cu-containing steam reforming catalysts are Cu⁰/Cu¹⁺.⁷

The Ni/Al and Co/Al LDH also undergo significant structural changes during the catalytic reaction. For the Ni/Al LDH, the only crystalline phase detected after reaction is NiO. Co/Al LDH forms an amorphous structure.

TPR data, shown in Figure 3, indicate that the reducibility of the metal is a key parameter in determining the catalytic activity.

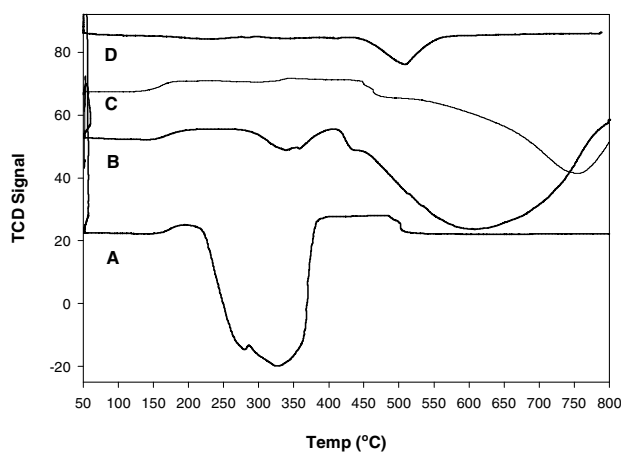


Figure 3. TPR data for A) Cu/Al, B) Ni/Al, C) Co/Al, and D) Mg/Al LDHs.

The lower reduction temperature of the Cu/Al LDH is consistent with the favorable reduction potential for Cu²⁺/Cu⁰ ($E^0 = 0.337$ V vs. SHE) compared with Co²⁺/Co⁰ ($E^0 = -0.28$ V vs. SHE) or Ni²⁺/Ni⁰ ($E^0 = -0.23$ V vs. SHE). TPR data also shows that very little reduction occurs with the Mg/Al LDH, and that the reduction temperature is highest compared to the other LDHs. This observation is consistent with the highly unfavorable reduction potential of Mg²⁺/Mg⁰ ($E^0 = -2.375$ V vs. SHE) and probably accounts for the observed lack of catalytic activity for this LDH.

Conclusions

Several LDH materials have been found to be active for steam reforming of methanol. The most favorable activity is observed with Cu/Al LDHs. Co/Al and Ni/Al LDHs also show catalytic activity; however, their activation temperature is higher and methanol conversions are lower. For the Ni/Al LDH, methanol decomposition appears to be the major reaction pathway. No activity was observed for the Mg/Al LDH. The TPR data indicate that the reducibility of the metals in the LDH is crucial in determining the extent of catalytic activity.

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